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8901 Wisconsin Avenue
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NMRI 95-02

February 1995



INTERIM CONTAMINANT LIMITS AND TESTING PROCEDURES FOR U. S. NAVY FLEET SODA LIME

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NMRI 95-02

The experiments reported herein were conducted according to the principles set forth in the current edition of the "Guide for the Care and Use of Laboratory Animals," Institute of Laboratory Animal Resources, National Research Council.

This technical report has been reviewed by the NMRI scientific and public affairs staff and is approved for publication. It is releasable to the National Technical Information Service where it will be available to the general public, including foreign nations.

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE February 1995	3. REPORT TYPE AND DATES COVERED Technical 9/92 - 9/94		
4. TITLE AND SUBTITLE INTERIM CONTAMINANT LIMITS AND TESTING PROCEDURES FOR U.S. NAVY FLEET SODA LIME.		5. FUNDING NUMBERS PE - 63713N/63713N PR - M0099/M0099 TA - .01A/.01B WU - 1052/1302		
6. AUTHOR(S) LILLO, R.S., A. RUBY, D.D. GUMMIN, W.R. PORTER, AND J.M. CALDWELL.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Medical Research Institute Commanding Officer 8901 Wisconsin Avenue Bethesda, Maryland 20889-5607		8. PERFORMING ORGANIZATION REPORT NUMBER NMRI 95-02		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Medical Research and Development Command National Naval Medical Center Building 1, Tower 12 8901 Wisconsin Avenue Bethesda, Maryland 20889-5606		10. SPONSORING/MONITORING AGENCY REPORT NUMBER DN17792		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) <p>Contamination of U.S. Navy Fleet soda lime (High Performance Sodasorb®), which contains indicator dye and is used for carbon dioxide absorption during diving, was suspected when an ammonia-like odor was reported during its use in August 1992. The Naval Medical Research Institute (NMRI) investigated the problem, which had a major impact on the U.S. Navy diving program when the Naval Sea Systems Command (NAVSEA) banned use of Sodasorb® and authorized Sofnolime® as an interim replacement. Significant amounts of ammonia (up to 30 ppm), ethyl and diethyl amines (up to several ppm), and various aliphatic hydrocarbons (up to 60 ppm) were detected during testing of both absorbents. The source(s) of the ammonia and amines are unknown, but it was thought that they may result from the breakdown of the indicator dye. Hydrocarbon contamination appears to come from the material making up the bucket. NAVSEA subsequently requested contaminant limits to insure procurement of soda lime without indicator dye that was safe for Fleet use. NMRI provided this guidance to NAVSEA in June 1994 in the document, "Interim Contaminant Limits for Procurement of Fleet Soda Lime." The present report describes the development of the test procedures in the NMRI guidance and provides background to the selection of contaminant limits contained therein.</p>				
14. SUBJECT TERMS ammonia, amines, carbon dioxide absorbent, diving, gas contamination, toxicology		15. NUMBER OF PAGES		16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

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ACKNOWLEDGEMENTS

This work was supported by Naval Medical Research and Development Command Work Unit Nos. 63713N M0099.01A-1052 and 63713N M0099.01B-1302.

The opinions expressed in this paper are those of the authors and do not reflect the official policy or position of the Department of Navy, Department of Defense, or the U.S. Government.

BACKGROUND

Soda lime is widely used as a carbon dioxide (CO₂) absorbent in underwater breathing systems and hyperbaric facilities. For the past few years, the U.S. Navy has purchased all of its soda lime for diving use from one manufacturer (W.R. Grace & Co., Lexington, MA) and packaged in high-density polyethylene, 5-gallon buckets with a net weight of 37 lb. The absorbent (High Performance Sodasorb®) contained ethyl violet, an indicator dye, to allow users to monitor by color change the decline in CO₂ absorbent ability of the soda lime with use. Contamination of U.S. Navy Fleet soda lime was suspected when an ammonia-like odor was reported during its use in August 1992 (1). The Naval Medical Research Institute (NMRI) investigated the problem, which had a major impact on the U.S. Navy diving program when the Naval Sea Systems Command (NAVSEA) banned use of Sodasorb® and authorized as an interim replacement Sofnolime®, another brand of soda lime with ethyl violet manufactured by Molecular Products Ltd., Essex, U.K. (2).

Soda lime testing by NMRI involved sampling from the headspace (gas space) inside closed buckets and from a test apparatus simulating actual use conditions. Volatile organic compounds were analyzed by gas chromatography and mass spectrometry; ammonia and amines were measured by infrared spectroscopy. Significant amounts of ammonia (up to 30 ppm), ethyl and diethyl amines (up to several ppm), and various aliphatic hydrocarbons (up to 60 ppm) were detected during testing of both Sodasorb® and Sofnolime®. Contaminants were slowly removed by gas flow and did not return. The source(s) of the ammonia and amines are unknown, but it was thought that they may result from the breakdown of the indicator dye during manufacture, processing, or storage. Hydrocarbon contamination appears to come from

the material making up the bucket. Details of the investigation by NMRI are contained in references (3-6).

At reference (7), NAVSEA requested that a military procurement specification be written to insure the exclusion of indicator dye from soda lime used for diving. The Naval Medical Research Institute responded to this request by providing NAVSEA with the document, Interim Contaminant Limits for Procurement of Fleet Soda Lime (5) and recommended that this guidance be included in any specification written by the Navy Experimental Diving Unit. NMRI also suggested that these limits be considered appropriate interim guidance for Fleet procurement until a formal specification could be developed, approved, and implemented. These contaminant limits reflect recommendations made by an in-house U.S. Navy working group (8). This report describes the development of the test procedures in reference (5) and provides background to the selection of specific limits for each of the contaminants.

CONTAMINANT LIMITS AND TESTING PROCEDURES

A copy of the Interim Contaminant Limits, which includes testing procedures recommended for procurement of Fleet soda lime, are contained in Appendix A. This copy is identical to that provided to NAVSEA in reference (5).

DEVELOPMENT OF TESTING PROCEDURES

Analytical procedures used in NMRI's investigation of contaminants in Fleet soda lime are described in detail in reference (6). Many of these procedures are complicated, time

consuming, and require expensive equipment and personnel with considerable experience in gas chromatography, mass spectrometry, and infrared spectroscopy. This was unavoidable because analyzing trace volatile organic compounds and reactive species (such as ammonia and amines) is inherently difficult and accurate data on the nature and quantity of the contaminants was needed to effectively evaluate the problem. However, in the development of contaminant limits to be used in the procurement of soda lime, a goal was to provide testing procedures that were less complicated, and lower in cost, but effective in insuring that the absorbent was chemically safe to the user. This approach would tend to avoid increased costs of the product associated with compliance with the limits and insure that testing was done correctly. As the difficulty of the testing increased, we believed that it would become less likely that the analysis would be done correctly. Thus, some of the testing methods described in this report are much different than those used in our investigation.

The tests described below for determining whether the product meets the specified contaminant limits are not a substitute for the detailed analysis needed to characterize fully the contaminants. In fact, NMRI will continue to compare the 2 sets of procedures as Fleet procurement of non-indicating soda lime begins, to evaluate the reliability of these interim screening procedures and the suitability of the limits. This is necessary as interim guidance is based on a number of assumptions, particularly the types of expected hydrocarbon contaminants and the relationship between indicator dye and ammonia and amines. Results will be used to refine the interim guidance when necessary, and the Fleet will be informed of any changes.

Ethyl violet dye analysis

A method was needed to insure that only dye-free soda lime be procured for diving use (7). At the start, NMRI thought that the best approach would be to provide 2 separate tests: 1) a simple procedure to confirm quickly that the absorbent was dye-free and 2) another method to quantify the amount of dye when it was present.

For the first test, the simplest procedure was to expose the absorbent to CO₂ and observe if any color change occurred. This would require a minimum amount of equipment and could even be done in the field. The initial setup consisted of a test tube trap that was loaded halfway with soda lime. A compressed gas cylinder of CO₂ with regulator and flowmeter was used to deliver a low flow of gas through the trap until the outflow gas had cooled, indicating no further reaction with the absorbent. The color of the soda lime in the sample trap was then compared to the color of soda lime in an identical trap (control) that had not been exposed to CO₂. The number of pellets that showed a color change relative to the control could be used to calculate the percentage that contained indicating dye. This test was repeated 3 times to deal with sample variability and was designated the qualitative dye test. Sensitivity of the qualitative test was estimated to be 0.0002% dye for each 1% of pellets that turn color based on an average dye concentration of 0.02% measured in 32 buckets of indicating soda lime (6). Errors in this assumption about the dye content of the few colored pellets would obviously affect the sensitivity estimate.

A quantitative dye test was needed to measure the amount of dye in soda lime. Initial development relied on the method of dye quantitation that is used by W.R. Grace & Co. and provided to NMRI. Procedures similar to those of W.R. Grace & Co. were also furnished to

NMRI by the O.C. Lugo Co., Inc. (Nyack, NY), which distributes Sofnolime® in the United States. This test measures the amount of ethyl violet indicator dye in soda lime on a weight/weight basis. Because dye determination is based on the dry weight of soda lime, the first step in this method was to determine the moisture content of the material. The soda lime was then dissolved in acid to convert the dye to its colored form, and the absorbence of the colored species measured with a spectrophotometer. The percent dye in the sample was calculated by applying a correction factor to the absorbence. The correction factor was defined in the method of W.R. Grace & Co. and stated to be derived from the molecular weight and absorptivity of the dye.

Work first focussed on duplicating the W.R. Grace & Co. method of dye analysis to determine its accuracy and usefulness for screening of Fleet soda lime. Accuracy of the procedure was checked by performing the test on dye-free soda lime to which known amounts of dye were added. Dye-free material was defined as absorbent experiencing no color change in any of the pellets during the qualitative dye test described above. Surprisingly, results indicated that measured dye concentrations were substantially lower than actual concentrations. In an attempt to resolve this problem, two sets of calibration standards were prepared over the range of dye concentrations expected in indicating soda lime. For one set of standards, dye (but no soda lime) was added to the reagents normally used for the test. For the other set, dye and dye-free soda lime were added. The amount of soda lime added was equivalent to 0.5 g dry weight, which is normally required in the analysis. Using these standards, calibration curves were constructed that differed considerably, particularly at low concentrations. Soda lime was observed to interfere with absorbence measurement so that

solutions with soda lime absorbed much less compared to the absorbent-free standards. The result was a fairly linear calibration curve for absorbent-free standards and a curvilinear function for standards with absorbent. The absorbent-free curve agreed closely with the correction factor in the method of W.R. Grace & Co.

A related problem was that the wavelength of peak absorbency shifted as the amount of dye was increased in the standards containing absorbent; this was not observed with absorbent-free standards. Furthermore, peak wavelength was different depending on which brand of soda lime was used, Sodasorb® or Sofnolime®. Thus, W.R. Grace & Co.'s technique of subtracting a baseline absorbence measured at 450 nanometers (nm) from the peak absorbence measured at 593 nm, although suitable for absorbent-free solutions, appeared inappropriate for analysis of soda lime. The effect of these problems was that dye measurements of soda lime, using W.R. Grace & Co.'s method, tended to be lower than actual concentrations, particularly at reduced dye levels.

For the preceding reasons, an alternate method was developed that used calibration standards to which soda lime was added. A separate set of standards was made for samples from each manufacturer using dye-free absorbent from that supplier. The sample size was also increased from 0.5 g (W.R. Grace & Co. method) to 4 g to improve the sensitivity and accuracy for the low dye measurements this procedure would be used. Each standard was scanned with the spectrophotometer from 400 to 700 nm and the absorbence of the peak maximum between 525 and 600 nm recorded; the baseline absorbence was taken at 700 nm. Calibration curves derived in this manner were generally not very linear, but allowed quantitation and reflected the absorbency differences of Sodasorb® and Sofnolime® (Fig. 1).

Because of the increased absorptivity due to the larger sample size, the calibration curve plateaued out at dye concentrations much above 0.020%. Therefore, this method is applicable only to low levels of ethyl violet in soda lime ($\leq 0.015\%$). For dye analysis of normal indicating soda lime, which was reported in reference (6), smaller sample sizes (e.g., 2 g) were used.

The accuracy of our method for very low dye concentrations was examined by analyzing samples we prepared in the laboratory by mixing a small percentage of dye-containing absorbent with dye-free material. Dye content of this prepared soda lime sample was estimated by multiplying the dye content of the indicating soda lime, as determined by our method, by the percentage of indicating pellets present. Differences between measured and estimated dye concentrations were $< 0.001\%$ (Fig. 2), confirming the usefulness of the technique at these concentrations.

Total hydrocarbons

The Naval Medical Research Institute's investigation implicated the 5-gallon, high-density polyethylene bucket used to package Fleet soda lime as the source of hydrocarbon contamination. All Sodasorb[®] was supplied in round buckets made by one supplier (Bennett Industries, Inc., San Fernando, CA). Sofnolime[®] was supplied either in round buckets (Fein Plastic Can Corp., currently a subsidiary of Bennett Industries) filled in the U.S. and similar to those used for Sodasorb[®], or in square containers (Blowmacan, Milton Keynes, U.K.) filled in the U.K.

The predominant hydrocarbon contaminants in soda lime were aliphatic species containing 4 to 13 carbon atoms/molecule (6). All major species found in round buckets

appeared to be saturated, except for small amounts of butene. The square buckets contained a number of compounds believed to be unsaturated or cyclic in nature based on results from mass spectrometry. In most cases, hydrocarbon concentrations were several ppm or less in terms of octane equivalents, although levels in a few buckets ranged up to approximately 60 ppm. A method was desired that would screen the headspace of buckets filled with soda lime for these types of contaminants. Initial requirements included the following: 1) the ability to detect ppm levels of hydrocarbons found in soda lime, 2) simplicity of operation, and 3) relatively low expense. Based on these factors, a photoionization detector (PID; model PI 101, HNU Systems Inc., Newton Highlands, MA) with a 10.2 eV light source was selected as the initial candidate analyzer for evaluation. This instrument is widely used in environmental work and on U.S. Navy nuclear submarines to measure total hydrocarbons in the atmosphere.

The PID is a portable instrument that consists of a meter assembly and a probe. A small fan in the probe draws the sample gas into an ion chamber that is exposed to an ultraviolet source. The source emits photons that have sufficient energy to ionize many trace contaminants, such as organics, but insufficient energy to ionize the major components of the atmosphere, such as N_2 , O_2 , and CO_2 . Any ions formed are detected via a pair of electrodes in the chamber across which a potential difference is maintained. The current generated is measured and displayed on the meter that is read by the operator.

Initially, three potential problems regarding the use of the PID for hydrocarbon screening of soda lime needed to be considered. The first problem was the sensitivity of the PID, which varies (over several orders of magnitude) with the chemical species and the amount of oxygen in the gas. The increased response when measurements are made in

oxygen-free gases is due to a reduction in the quenching of ions by oxygen. This quenching effect should not be a problem, as all PID calibration and measurement were to be done in an air background. In view of the nature of the hydrocarbons involved (primarily saturated aliphatic species), the variation in PID sensitivities was not expected to be significant for the round buckets of either Sodasorb[®] or Sofnolime[®], with one exception (9-10). The PID should be perhaps twice as sensitive to the one unsaturated species, butene, compared to octane in view of butene's lower ionization potential. In the case of the square Sofnolime[®] buckets, the PID should also be more sensitive to the unsaturated or cyclic compounds that were present. The second problem was that the PID responds to many types of chemicals including non-hydrocarbons. Although the only other known contaminants were ammonia and ethyl and diethyl amine, their effect on the PID needed to be evaluated. The third concern was that PID measurements have been reported to be influenced by high humidity, although water vapor itself is not detected (11). The manufacturers' product descriptions for both brands of soda lime (Sodasorb[®] and Sofnolime[®]) indicate a maximum water content of 19%; this was confirmed by NMRI during measurement of the ethyl violet dye. Whether this amount of water would interfere with PID measurements of bucket headspaces was unknown.

The relatively low sensitivity that the PID is reported to have for ammonia (10) was verified by NMRI using primary standards containing up to 30 ppm ammonia. The PID sensitivity for ammonia was well over an order of magnitude lower compared to octane when expressed as PID value/ppm of analyte. Therefore, the PID should be relatively unaffected by the ammonia levels found in soda lime (up to 30 ppm). However, it was expected to respond strongly to the amines based on their low ionization potentials, which was confirmed in the

lab using amine standards up to 10 ppm. For both amines, it took over 5 min for the PID to stabilize at full deflection. However, when measurements were taken at 1 min, PID sensitivities for the 2 amines were similar to that for octane. It was still necessary to determine whether this slow response and the relatively low amine concentrations would minimize interference by the amines with hydrocarbon screening.

The effect of water vapor on PID performance was examined by measuring octane in air over a range of relative humidities. The experimental setup allowed simultaneous octane measurements with the PID and an FTIR spectrophotometer (model 1600 FT-IR, Perkin Elmer Corp., Norwalk, CT) which is fully described in reference (6). Both instruments were calibrated using a 10 ppm octane, balance air, primary standard. Some testing used a precision gas divider (STEC model SGD-710, Horiba Instruments, Inc., Ann Arbor, MI) that allowed blending of gas mixtures from 0 to 100% of the original concentration. This device has been previously shown to be linear to within the manufacturer's specification of $\pm 0.5\%$ of full scale using ppm levels of several volatile organic compounds (12). Our FTIR analysis of octane had been shown to be accurate to ± 0.5 ppm up to 10 ppm octane, with or without water vapor (6), and thus was used as a reference to determine the error of the PID. All PID data was corrected for the weak response to hydrocarbon-free air (typically 0.4 to 0.9 ppm octane equivalents) by subtracting this value, which was measured frequently during testing, from the actual PID reading.

Initial testing using the STEC device blended a 10 ppm octane, balance air, primary standard with dry diluent hydrocarbon-free air. Both PID and FTIR measurements were within 0.7 ppm of each other at all concentrations (Fig. 3), a difference that is within the combined

analytical error of both instruments. Actual testing of the effect of water vapor on the PID involved diluting the 10 ppm octane standard with either humidified air or humidified 10 ppm octane, with a total flow directed through the FTIR of 5 l/min. Gas was humidified by using a water bubbler described in reference (6). The first set of tests used the STEC device with humidified air as the diluent; here both the water content and the octane concentration varied as the blending ratio was changed. However, the STEC appeared to remove some water from the gas as relative humidities were lower than would be expected and desired. Therefore, the STEC was omitted in the second series of tests where a needle valve was used to control the amount of dry octane that was blended with humidified octane. This method achieved higher relative humidities while maintaining octane concentrations at 10 ppm. Dew points of sample gas were measured using a dew point hygrometer (model Hygro-M1; General Eastern Instruments, Woburn, MA). These measurements and those of ambient temperature (Tele-thermometer, model 2100; Yellow Springs Instrument Co., Yellow springs, OH) allowed determination of relative humidity.

Results demonstrated that PID analysis of up to 10 ppm octane in air could be significantly affected by water vapor. As relative humidities were increased from 0 to 85%, PID measurements declined in linear fashion down to 40% of expected reading (i.e., FTIR value); linear regression results (Quattro Pro for Windows, version 5.00; Borland International Inc., Scotts Valley, CA) are included (Fig. 4). Relative humidities of the bucket headspace measured from a number of buckets of Sodasorb® and Sofnolime® ranged from 66 to 86% (Table 1). It appeared, therefore, that humidity could potentially have a major effect on the reliability of PID screening soda lime buckets for hydrocarbon contamination. Bucket

humidity values were based on dew points measured by opening each bucket's pour spout, immediately inserting the hygrometer probe several inches into the bucket, and recording the dew point after instrument stabilization, typically within 10 s. All of these buckets had been previously opened and sampled so that they were only partially filled. However, in the case of Sofnolime[®], most of the buckets had over half the absorbent left. Such prior sampling was not expected to have a major effect on dew point determination unless the bucket was nearly empty, had been repeatedly opened, or had not been sealed properly after use. One or more of these factors probably explains the one low value of 66% that was obtained.

Final evaluation of the accuracy of the PID involved taking readings from all Sodasorb[®] and Sofnolime[®] buckets remaining from NMRI's investigation. Unfortunately, only a few of the Sodasorb[®] buckets were left for testing. All but 2 buckets contained soda lime with indicator dye. The simplest sampling approach was chosen for testing: the pour spout on top of the bucket was opened, the PID probe immediately inserted, and the meter response observed. As before, the PID was calibrated with a 10 ppm octane, balance air, primary standard; thus, PID readings were in terms of octane equivalents. All buckets were analyzed after being stored closed at > 18 °C for at least 3 days. The greatest potential problem with this method was that the concentration of the headspace started declining immediately as ambient air moved into the bucket and hydrocarbons moved out via convection/diffusion. Thus, the PID response peaked within 10 s and then declined. However, instrument response time (less than 3 s to 90% of full scale deflection), specified by the manufacturer (10) and confirmed by experience of NMRI personnel, would appear adequate in this application. Such a quick bucket response should minimize any interference by the amines, which take much

longer for equilibration. An alternative of inserting the PID probe through an air-tight seal into a closed bucket and sampling without allowing outside air to enter was ruled out. This procedure may have drawn intra-bucket pressure below atmospheric pressure, which would have affected the PID readings.

Maximum PID values for buckets tested on two different days are given in Table 1. These were compared to two soda lime measurements reported previously and made with the FTIR as contaminants were flushed out of the soda lime (6): 1) the maximum octane value representing a measurement of total hydrocarbons and 2) the sum of the maximum octane, ethyl amine, and diethyl amine values (Table 1 and Fig. 5). The latter would represent the maximum concentration of the three major contaminants, excluding ammonia, found in soda lime. Ammonia was ignored due to its insignificant effect on the PID. For purposes of data workup, all FTIR measurements below our previously defined reporting limits were set equal to their actual values, as done with earlier modeling (6).

Differences between PID and the two FTIR measurements were on average no more than 1 ppm, although substantial variability existed as reflected by the range and standard deviation associated with the values. Much of the variability undoubtedly relates to the decreased accuracy associated with low PID and FTIR measurements (6). Unfortunately, low hydrocarbon contamination characterized most of the buckets that were tested. A few instances where PID values exceeded FTIR octane levels by over 2 ppm may be explained by the higher concentrations of butene, which produces a strong PID response (e.g., buckets SL34 and SL35). Correlation between PID and the combined octane and amine FTIR measurement was determined using linear regression and found to be poor on both days of

PID testing with r^2 's of 0.18 and 0.51. Excluding the 7 buckets with total amine values > 2 ppm, improved correlation with r^2 increasing to 0.57 and 0.77, respectively with regression slopes (standard deviation) of 1.3 (0.2) and 1.8 (0.2). A slope of 1 would signify agreement between the PID and FTIR. The problem was that buckets with high amine levels generally had PID readings lower than expected, based on total contaminants (Fig. 5), suggesting the amines contributed less, on a relative basis, than hydrocarbons to the PID bucket response. However, this issue should disappear if the absorbent passes the other tests as dye-free soda lime should have little, if any, amines.

The degree of agreement between PID and FTIR, although limited, is notable in view of the potential problems discussed above. Despite sampling through an opened pour spout and the presence of high humidity, results suggest that the PID may be a useful device for hydrocarbon screening of soda lime buckets over the reported concentration ranges. Unfortunately, we were unable to determine PID reliability for buckets with hydrocarbon levels near or above the recommended limit or for species significantly different from those found thus far. For simplification, actual procedures for PID screening of soda lime (Appendix A) omit the weak response to hydrocarbon-free air discussed earlier. This should have a minimal effect on the accuracy of the test.

Ammonia and amines

During NMRI's investigation of soda lime contaminants, FTIR analysis with a 20-meter gas cell was used to measure ammonia, ethyl amine, and diethyl amine in gas flowing through a bed of soda lime. Procedures and system performance are detailed in reference (6). Unfortunately, reliable alternatives to this complicated analysis could not be identified.

Therefore, these methods are used in the Interim Contaminant Limits.

SELECTION OF CONTAMINANT LIMITS

Safe diving limits for the observed contaminants are unknown due to the wide range of possible operational conditions (e.g., pressure, flow, temperature, closed vs. open circuit use, dive duration) and the complex nature of the contaminant mixtures. However, existing exposure limits for chemicals in settings other than diving provide some guidance. The American Conference of Governmental Industrial Hygienists (ACGIH, reference (13)) recommends a threshold limit value-time-weighted average (TLV-TWA) for ammonia of 25 ppm for an 8-hour period and a TLV-short-term exposure limit (TLV-STEL) of 35 ppm for 15 min for application in standard civilian industrial settings. The National Aeronautics and Space Administration in cooperation with the National Research Council has recently specified new spacecraft maximum allowable concentrations (SMACs) of 30 ppm and 20 ppm of ammonia for 1 h and 24 h continuous exposure, respectively (14). These ammonia limits were chosen primarily to avoid irritation to the mucous membranes of the eyes and upper respiratory tract. Corresponding TLV-TWA values for both ethyl and diethyl amine are 5 ppm. TLV-STEL values for both amines are 15 ppm; new SMAC limits are not currently available for amines. Guidance for the amines is also based on eye and respiratory irritation, although their lower limits reflect their much stronger effects. Recommended TLV-TWA values for most saturated hydrocarbons are relatively high. However, the value for hexane, the most toxic of the group, is set at 50 ppm because of its effects on the nervous system. For comparison, the TLV-TWA for octane is 300 ppm based on narcotic and irritative effects.

The Naval Medical Research Institute's investigation suggested that contaminant levels measured in the laboratory may represent the upper exposure levels during diving, if minimal dilution occurs in a diving rig (6). However, diver exposure levels could be significantly less if substantial dilution of contaminants occurs during use. The worst case exposure to contaminants from soda lime during actual diving was estimated by NMRI (15) to be 370 min of continuous exposure, with 3 exposures per week, based on current U.S. Navy diving practices. This is less than the 8 h/day, 40 h/week exposure scenario used to develop the TLV-TWA values.

In view of the preceding considerations, the in-house U.S. Navy working group made a number of recommendations in reference (8) regarding the maximum permissible concentrations of known contaminants in Fleet soda lime. Such concentrations would be based on measurements made in the laboratory. The maximum permissible concentration for ammonia in soda lime was recommended to be 10 ppm, 40% that of the TLV-TWA value, in consideration of the range in possible conditions to which a diver using soda lime might be exposed. Because of the similarity of effects of ethyl and diethyl amines, a limit of 5 ppm was recommended as appropriate for the total of both species, assuming additive effects (13). Both the ammonia and amine limits were believed easily achieved by elimination of all ethyl violet indicating dye based on NMRI's findings (6).

Absence of dye was to be checked using either the qualitative or the quantitative dye test. The qualitative test was arbitrarily defined as negative if less than 5% of the pellets showed a color change as detailed in Appendix A. Based on the estimated sensitivity of the test made earlier, a negative test would be expected when dye concentration is less than

0.001%. This limit would allow for accidental contamination of a batch of dye-free absorbent by a small amount of pellets from a previous production batch of dye-containing material. In cases where more dye is present, the quantitative test would be required where the maximum permissible concentration of dye was defined to be less than 0.005%, the amount that could be reliably quantified.

The need for a clean container that would not add significant contaminants to soda lime was affirmed by the working group. We chose 10 ppm as the container limit for total hydrocarbons based on the relatively low toxicity of the hydrocarbon species found in the buckets. Our investigation had shown that the majority of high-density polyethylene buckets tested by NMRI and used in the past for soda lime would have met this standard. However, this limit would have been exceeded by the few buckets that had much higher than average hydrocarbon levels. A more restrictive hydrocarbon limit was not seen necessary for diver safety and would have undoubtedly increased container costs for the supplier and, thus, for the Fleet.

REQUIRED AND NON-REQUIRED TESTING

The primary goal of defining contaminant limits and testing procedures for Fleet soda lime was to insure that the absorbent is safe for diving. Secondary aims included minimizing any additional costs associated with the contaminant and testing requirements and simplifying the approach, where possible. Toward these ends, a series of 4 tests were defined (Appendix A) for screening Fleet soda lime. When the required qualitative dye test is negative, manufacturer testing for ammonia, diethyl amine, and ethyl amine is not mandatory and dye

does not have to be quantified. The assumption is that these 3 contaminants would not be present at levels above the maximum permissible concentrations if dye is absent, for reasons discussed previously. However, when the qualitative dye test is positive, dye must be quantified and ammonia and the amines must be analyzed as the potential for unacceptable dye content and associated contamination would exist. The manufacturer would also be responsible for providing a safe container by being required to test for total hydrocarbons. Regardless of which testing is required, reference (5) specifies that the manufacturer is responsible for meeting the contaminant limits defined therein.

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Table 1. Soda lime bucket test data.

NMRI Bucket Code/ Bucket Type	Relative Humidity (%)	FTIR Maximum Octane (ppm)	FTIR Maximum Amines (ppm)	FTIR Maximum Contaminants (ppm)	5/19/94 PID (ppm octane)	5/26/94 PID (ppm octane)
Sodasorb®						
BB1/R	84.4	1.1	4.1	5.2	0.6	0.6
BB3/R	76.5	0.3	1.5	1.8	0.6	0.2
BB4D/R	66.1	5.0	1.9	6.9	8.1	11.6
G01/R	78.5	0.5	1.2	1.7	0.7	0.4
G02/R	80.9	0.2	2.2	2.4	0.9	0.4
G10/R	80.4	0.9	1.2	2.1	0.7	0.0
C1/R	84.0	0.7	5.1	5.8	1.3	6.0
Sofnolime®						
SL3/R		0.6	1.0	1.6	0.7	0.6
SL12/R		0.7	2.1	2.8	1.3	1.4
SL13/R	80.9	0.7	1.9	2.6	2.1	1.6
SL14/R		0.5	1.1	1.6	3.1	2.4
SL15/R		0.8	0.9	1.7	1.1	0.8
SL16/R		0.7	1.3	2.0	1.1	1.1
SL17/R		0.7	1.1	1.8	4.9	4.2
SL18/R		0.6	2.0	2.6	2.7	2.6
SL19/S	82.8	0.2	1.0	1.2	0.7	0.1
SL20/S		0.2	0.7	0.9	-0.4	0.1
SL21/S	85.4	0.2	4.5	4.7	0.7	1.9
SL22/S	84.3	0.2	2.4	2.6	0.1	0.3
SL23/S		0.4	0.6	1.0	0.5	-0.1
SL24/S	86.4	0.3	0.5	0.8	0.7	0.3
SL25/S		0.2	1.2	1.4	0.9	0.1

NMRI Bucket Code/ Bucket Type	Relative Humidity (%)	FTIR Maximum Octane (ppm)	FTIR Maximum Amines (ppm)	FTIR Maximum Contaminants (ppm)	5/19/94 PID (ppm)	5/26/94 PID (ppm)
SL26/S		0.2	1.6	1.8	0.8	0.1
SL27/S	79.8	0.6	1.0	1.6	2.5	2.7
SL28/S	82.3	0.4	0.8	1.2	2.5	2.1
SL29*/S	82.4	0.3	0.8	1.1	1.5	0.8
SL30/S	80.2	0.2	0.7	0.9	0.7	0.1
SL31*/S	84.4	0.2	1.5	1.7	1.9	1.0
SL32/R	79.8	0.6	1.3	1.9	2.9	2.2
SL33/R		0.4	2.0	2.4	1.9	0.6
SL34/R		0.6	3.4	4.0	5.0	3.0
SL35/R		0.6	2.0	2.6	6.5	3.0
Mean (SD)	81.1 (4.5)	0.6 (0.8)	1.7 (1.1)	2.3 (1.5)	1.9 (1.9)	1.6 (2.3)
Range	66.1 to 86.4	0.2 to 5.0	0.5 to 5.1	0.8 to 6.9	-0.4 to 8.1	-0.1 to 11.6
N	18	32	32	32	32	32
1. Bucket type: R = round, S = square. 2. *: non-indicating soda lime. 3. Maximum contaminant value: sum of the concentrations of octane, ethyl amine, and diethyl amine. 4. Blank relative humidity values indicate no measurement made. 5. Manufacturer lot number and production date for each bucket are given in reference (6)						

FIGURE LEGENDS

Figure 1. Dye calibration curves for Sodasorb® and Sofnolime® based on standards containing dye-free absorbent. A high and low range set of standards were run for each absorbent. Delta A (absorbance difference) was measured using a spectrophotometer as described in text.

Figure 2. Measured dye concentrations at low levels compare well with calculated concentrations based on the percentage of dye-containing soda lime added to a test sample of dye-free material. Results confirm the usefulness of the NMRI dye analysis technique at these concentrations.

Figure 3. PID vs. FTIR for dry octane using STEC device to dilute a 10 ppm octane in air standard. The difference between the 2 measurements is within the combined analytical error of the 2 instruments. The line on the graph represents a perfect 1 to 1 agreement between the readings.

Figure 4. Increasing relative humidity from 0 to 85% produced a linear decline in PID reading down to 40% of expected (i.e., FTIR value). Actual octane concentrations ranged up to 10 ppm in air. Results are from 2 days of testing using the STEC device one day and a needle valve another day to divide the gas mixtures. Linear regression results for the combined data are included and the regression line plotted.

Figure 5. PID measurement (made on 19 May 94 (5a) and 26 May 94 (5b)) of soda lime buckets vs. maximum contaminants of the same bucket previously measured with FTIR. The maximum contaminant value is defined as the sum of the concentrations of octane, ethyl amine, and diethyl amine. The line on the graph represents a perfect 1 to 1 agreement between the values. Buckets with high amine levels (> 2 ppm total amines) tended to have PID readings lower than expected based on total contaminants.

Figure 1

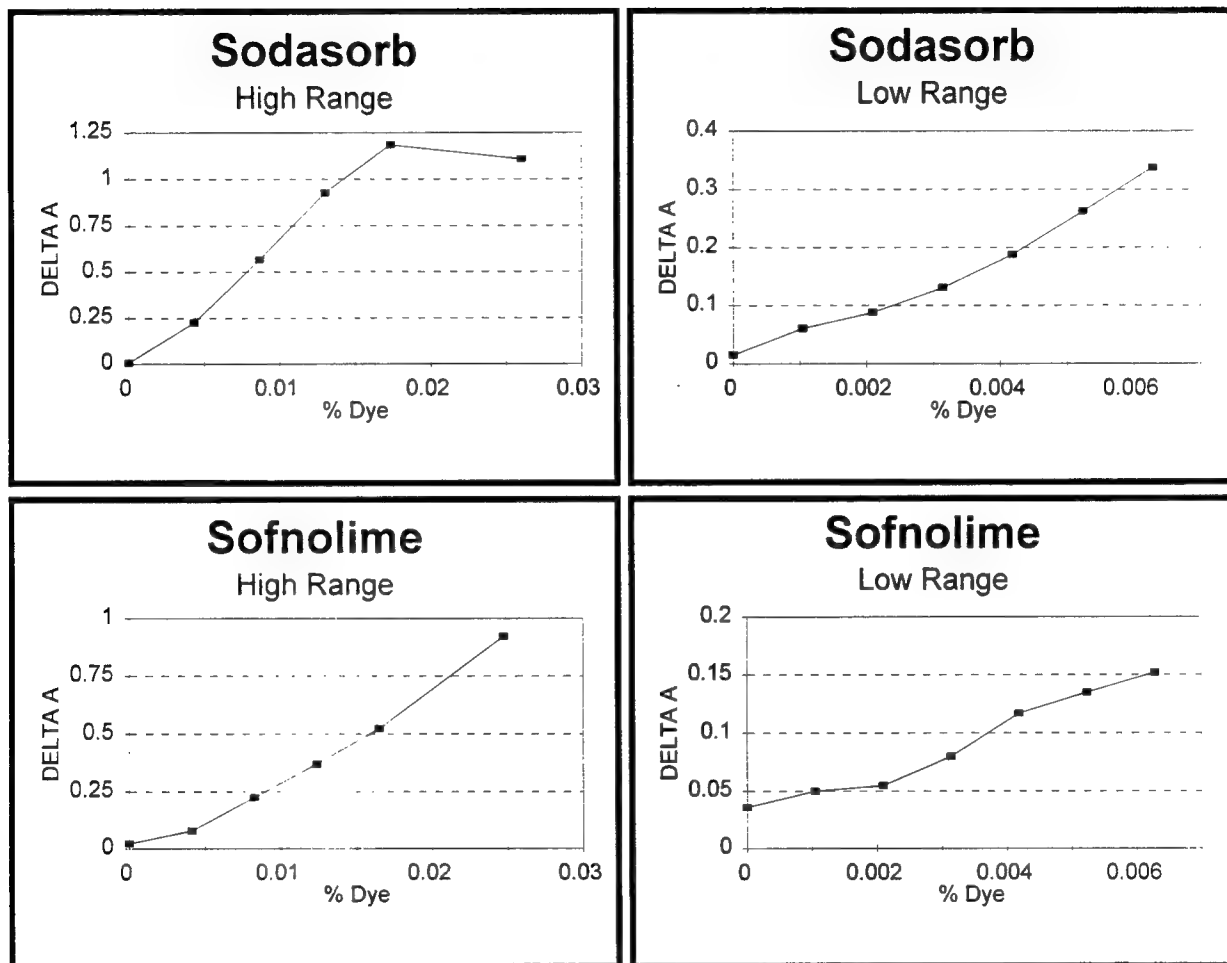


Figure 2

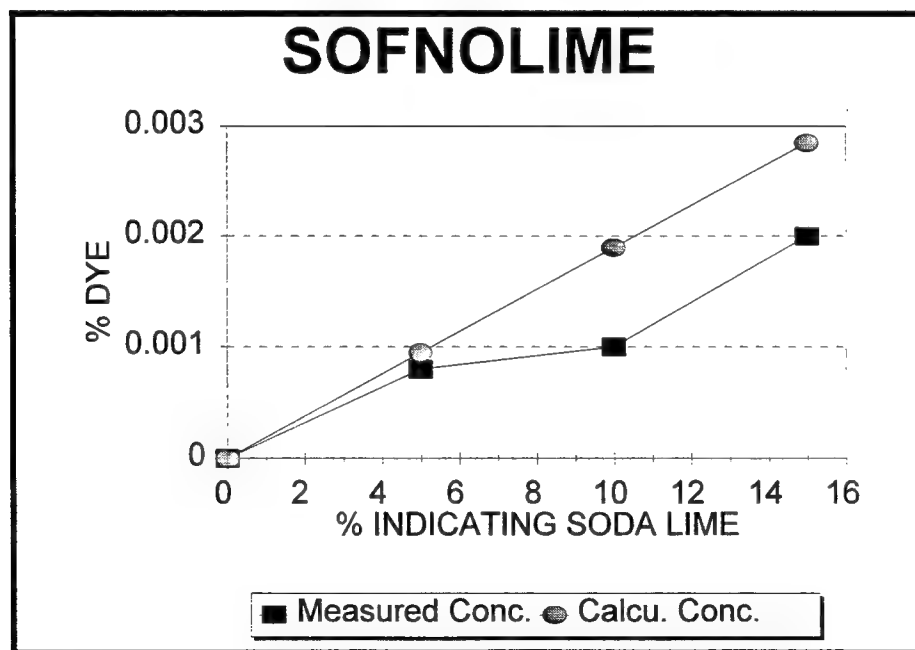
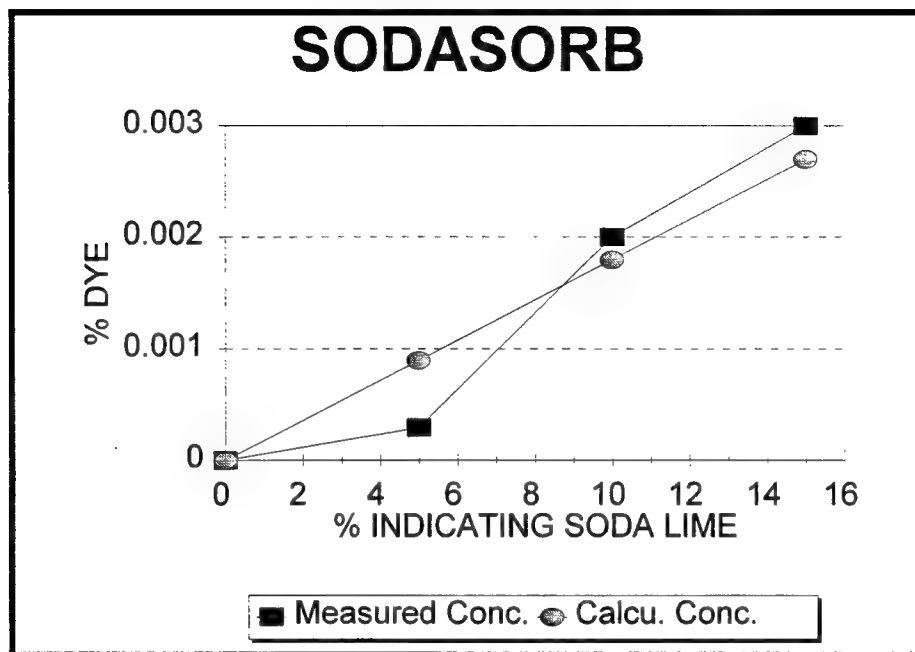


Figure 3

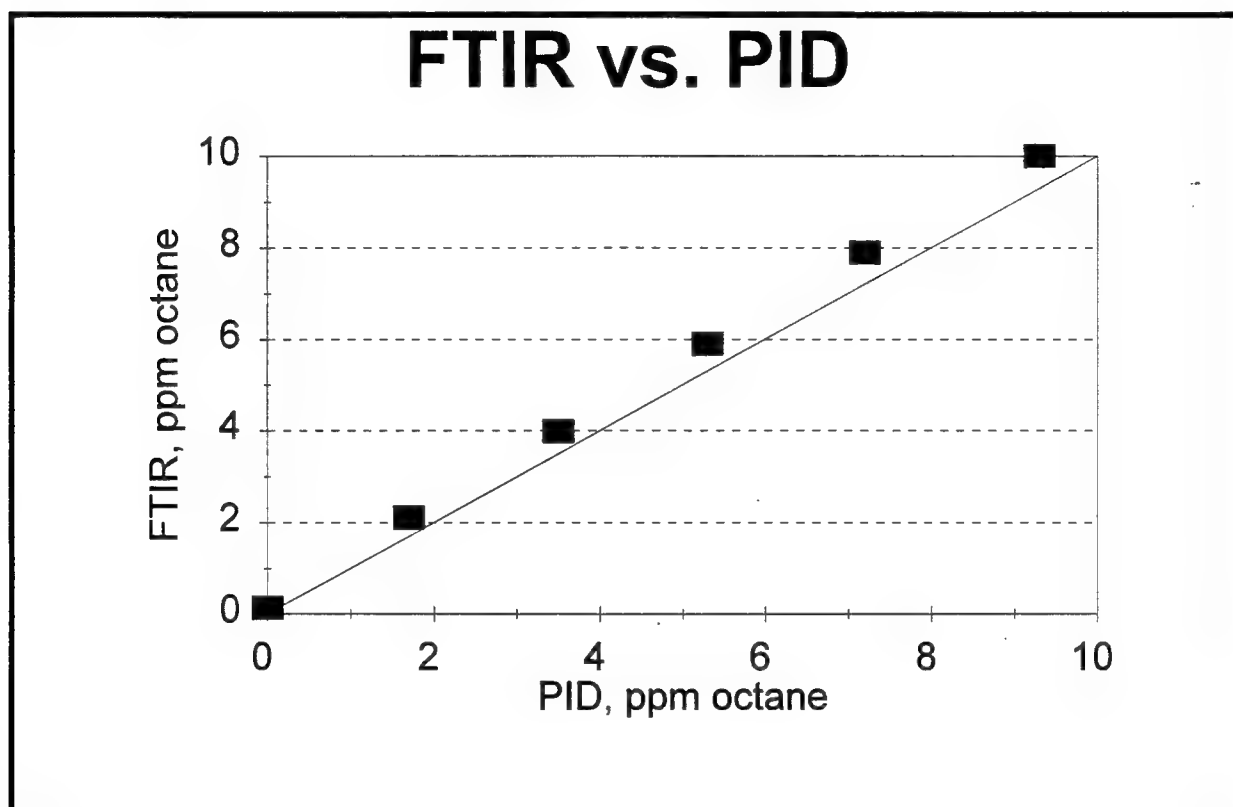


Figure 4

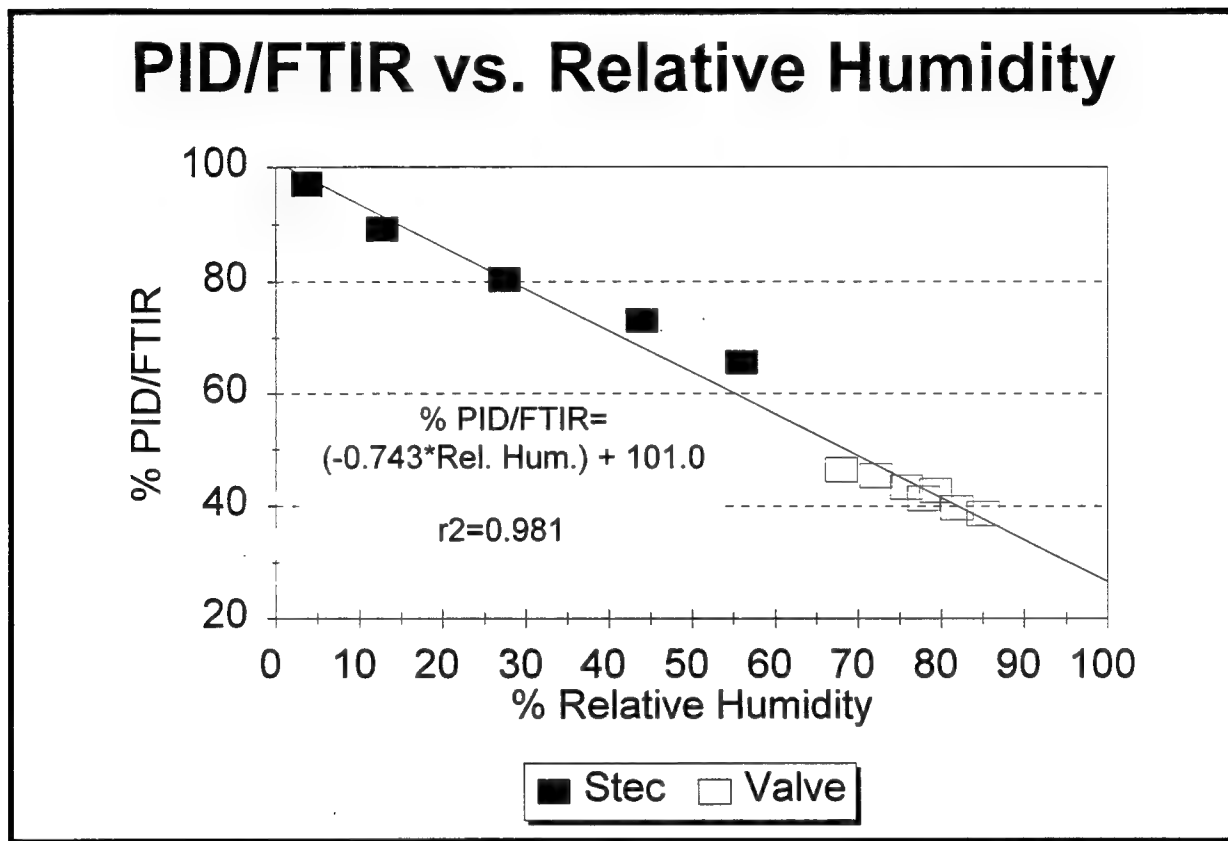


Figure 5A

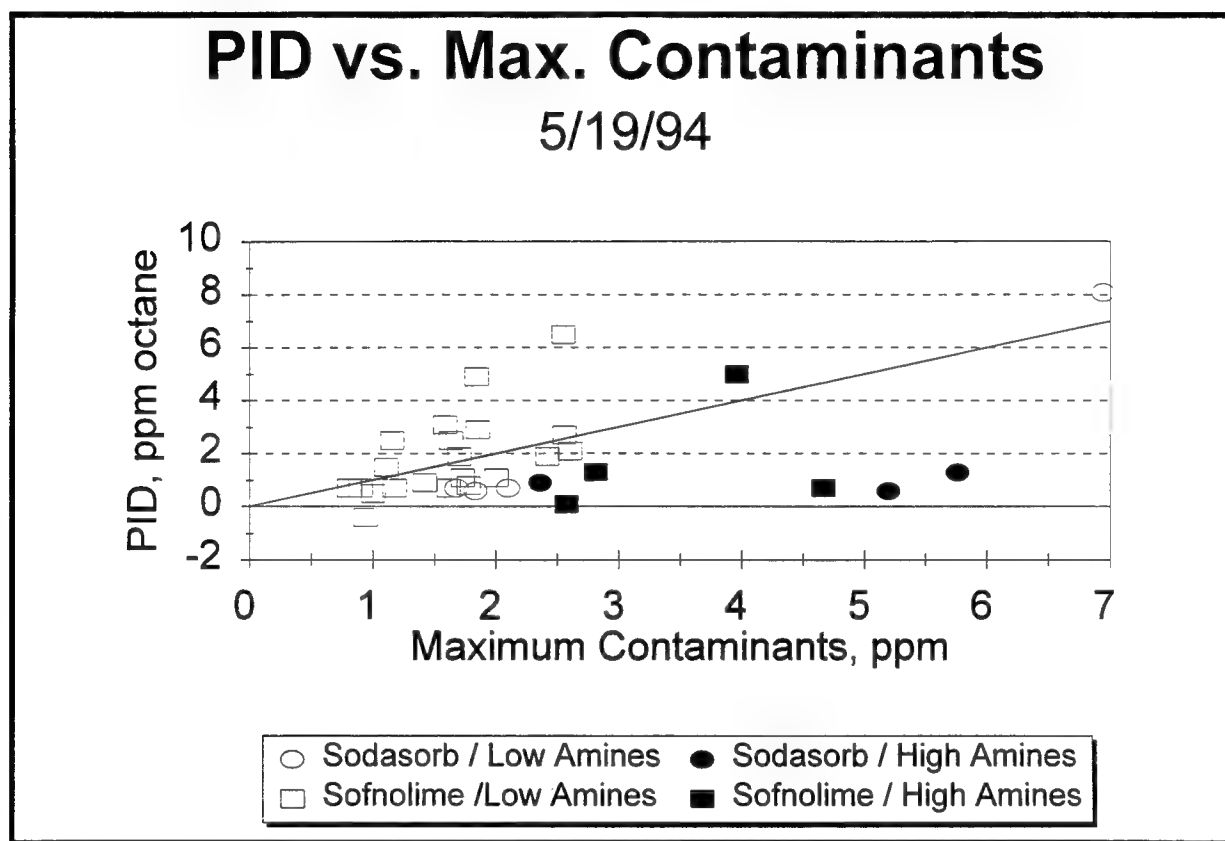
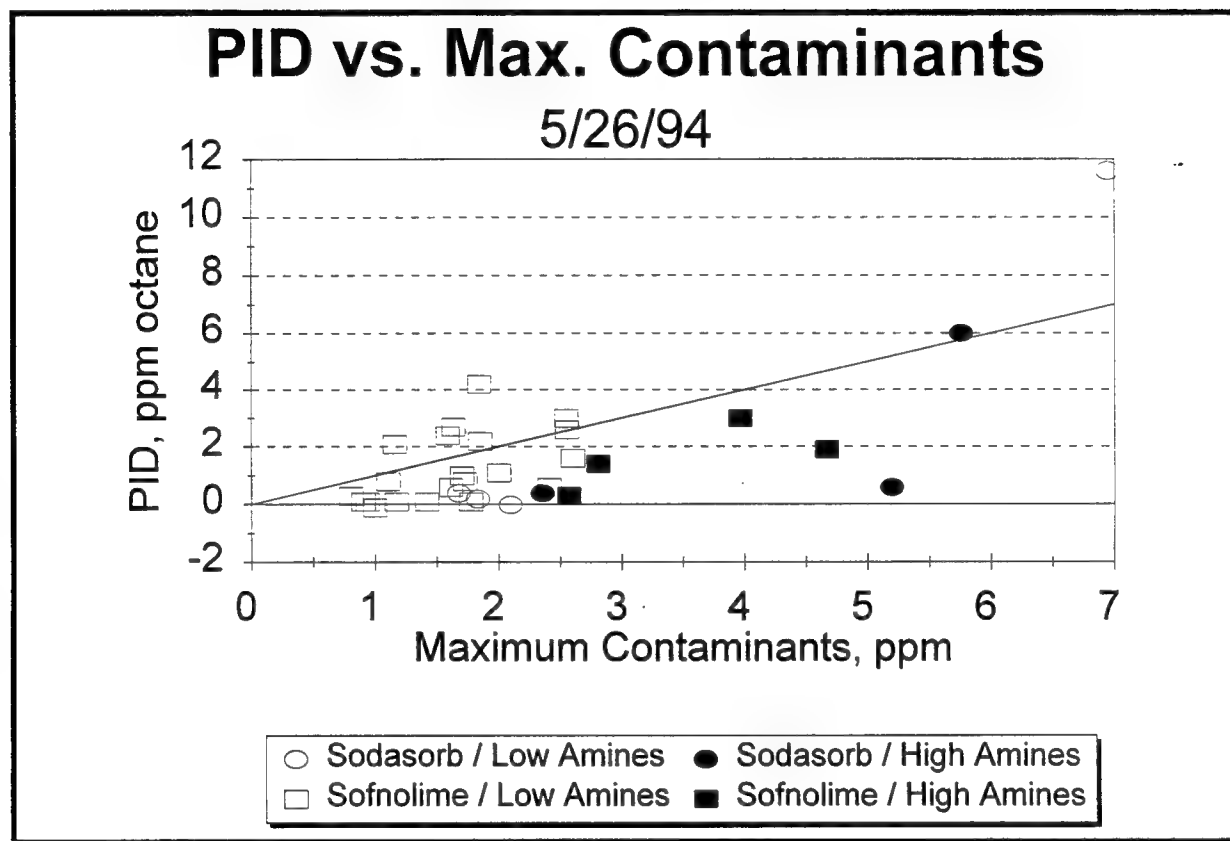


Figure 5B



APPENDIX A
INTERIM CONTAMINANT LIMITS FOR PROCUREMENT OF FLEET SODA LIME

This is identical to guidance provided to NAVSEA in reference (5) and includes 2 additional figures (Figs. 1 and 2) at the very end of the appendix.

Written in format for inclusion in the procurement specification

CONTAMINANTS

Constituents other than calcium hydroxide, sodium hydroxide, potassium hydroxide, and water shall not exceed the limits specified in Table X. No ethyl violet indicator dye will be present.

Table X - Chemical Composition

<u>Constituent</u>	<u>Maximum permissible concentrations</u>
Ethyl violet	none (<0.005%)
Total hydrocarbons	10 ppmv (octane equivalents)
Ammonia	10 ppmv
Diethyl amine and ethyl amine	5 ppmv (sum of both)

Absence of indicator dye shall be qualitatively confirmed by the test in XX1.

Total hydrocarbons will be measured as defined in XX2.

When the qualitative dye test (XX1) is **NEGATIVE**, manufacturer testing for ammonia, diethyl amine, and ethyl amine is not required. However, samples may be analyzed by the tests in XX3 and XX4 to insure compliance with Table X.

When the qualitative dye test (XX1) is **POSITIVE**, the following testing is required: 1) testing defined in XX3 to quantify the amount of dye in the sample and 2) testing defined in XX4 to quantify the amount of ammonia, diethyl amine, and ethyl amine in the sample. Samples showing a positive dye test (in XX1) are acceptable if they meet limits in Table X.

XX1. Qualitative detection of ethyl violet dye in soda lime.

The presence of indicating dye in soda lime shall be determined by flowing CO₂ over a sample and visually observing the color change.

XX1.1. Equipment.

1. In-line glass trap, configured as in Fig. 1 using:

- a) Pyrex test tube, 25 mm outer diameter, 150 mm long, VWR #60815-228
- b) Stopper, 2 hole, #5, VWR# 59582-202
- c) Polyethylene tubing, 5 mm outer diameter, VWR #63018-868.

An equivalent configuration is acceptable.

2. Compressed gas cylinder of CO₂ (99% or greater) with a regulator and flowmeter for delivery at a rate of 100 ml/min.

XX1.2. Procedure.

1. Place 10 +/- 1 g (approximately one-half the trap volume) of soda lime to be tested in each of two traps. Keep one as a control visual standard.
2. Flow CO₂ at approximately 100 ml/min through the sample trap for 2 minutes minimum until outflow gas has cooled to room temperature.
3. Compare the color of the soda lime in the sample trap to that of the soda lime in the control trap. Count the number of pellets that show ANY color change. The sample fails the test if 5% or more of the pellets show a color change. The sample passes the test if less than 5% of the pellets show a color change.
4. Repeat steps XX.1.2.1-3 two more times so that a total of 3 tests are completed from the same soda lime.
5. If at least 2 out of 3 tests fail, the dye test is POSITIVE. If at least 2 out of 3 tests pass, the dye test is NEGATIVE.

XX2. Total hydrocarbon analysis of container headspace.

This test measures the total hydrocarbon concentration of the headspace (gas space) inside filled soda lime containers as supplied by the manufacturer. A portable photoionization detector is used for measurement although a method of equivalent sensitivity may be used in place of that described.

XX2.1. Equipment.

1. Model PI 101 portable photoionization detector (PID) with 10.2 ev lamp; HNU Systems Inc., Newton, MA; or equivalent.
2. One gravimetric primary standard for PID calibration, prepared in hydrocarbon-free air: 10 ppm octane, certified to $\pm 2\%$ relative and in a pressurized cylinder.
3. Suitable high-purity regulator (with stainless steel diaphragm, 0-50 psig delivery pressure) for calibration gas. A 5 ml plastic syringe barrel, or equivalent, should be attached to the outflow of the regulator using a short piece of plastic tubing as a butt connector taking care to minimize contact of this tubing with the flowing gas.

XX2.2. Procedures.

1. All testing will be done on previously unopened containers filled with soda lime and stored for a minimum of 3 days at 18 to 25 C immediately preceding hydrocarbon measurement.
2. Purge octane cal gas regulator 3 times by alternately pressurizing and de-pressurizing to atmosphere. Then, open cylinder valve and adjust delivery pressure to 5-10 psig.
3. Disconnect meter from battery charger. Check battery power by turning meter to "BATT". Meter should read in green.
4. Turn meter to "STANDBY". Wait 2 minutes, then adjust meter to 0 with "zero" knob while probe is positioned in syringe barrel.
5. Turn meter to "0-20" range. Turn on flow from the octane calibration gas so the flow can be faintly heard; some adjustment of the regulator delivery pressure may be necessary. Probe should remain in syringe barrel. When needle stabilizes, adjust reading to the ppm of the octane mixture with "SPAN" knob.
6. Recheck zero in "STANDBY" and repeat steps #4-#6 if meter does not return to zero. Close gas cylinder valve and delivery knob and outflow valve on regulator.
7. With the PID in "STANDBY", move to location of test containers. Zero meter in "STANDBY" with PID meter and probe beside container.

8. Switch to "0-20" range, open the pour spout on the soda lime container, and immediately insert the PID probe into the spout so that the probe is angled down away from the opening and less than 1 inch above the absorbent. Record the maximum meter reading to the nearest 0.1 ppm (meter reading will slowly decrease as hydrocarbon vapor leaves and air enters the container). Total hydrocarbon concentration will be reported to the nearest 0.1 ppm in octane equivalents and shall not exceed the limit in Table X.

XX3. Quantitative determination of ethyl violet in soda lime.

This test is applicable only to low levels of ethyl violet in soda lime ($\leq 0.015\%$).

XX3.1. Principle.

This test measures the amount of ethyl violet indicator dye in commercial soda lime on a weight/weight basis. Because dye determination is based on the dry weight of the soda lime, the first step in the method is to determine the moisture content of the material. The soda lime is then dissolved in acid to convert the dye to its colored form, and the absorbence of the colored species is measured to allow calculation of its concentration. A method of equivalent sensitivity and accuracy may be used in place of that described.

XX3.2. Equipment.

1. Analytical balance accurate to ± 1 mg.
2. 100 ml volumetric flasks.
3. Plastic weighing dishes.
4. Stirring hot plate with Teflon coated stir bars.
5. A.C.S. reagent grade glacial acetic acid, diluted to 50% v/v with distilled water.
6. Spectrophotometer, scanning, Shimadzu UV-160, or equivalent.
7. Standard cuvettes, 10 mm, VWR 58017-847 or equivalent.
8. Vacuum oven, Fisher #13-264A or equivalent.
9. Weighing bottles, Kimax #7-4300-70 or equivalent.
10. Pipet, 10 ml.
11. Ethyl violet, CAS no. 2360-59-2, Aldrich #22,884-2 or equivalent.

All equipment can be obtained from any general scientific supply company.

XX3.3. Procedure.

1. Percent moisture.

The moisture content is determined for the sample to be analyzed and for a blank sample from the same manufacturer that is free of dye as determined by a negative dye test in XX1.

- a. Weigh 20 ± 1 g of soda lime to the nearest 1 mg in a covered weighing dish.
- b. Place the dish in either a vacuum oven or standard laboratory oven at 100 ± 2 C and remove the cover. Maintain a partial vacuum or gentle inert gas purge to prevent the soda lime from reacting with atmospheric CO_2 .
- c. Heat the sample for 2 hours \pm 5 min. Replace the cover on the weighing dish before removing it from the vacuum oven. Allow the sample to cool to room temperature and re-weigh.
- d. Calculate the percent moisture as follows:

$$\% \text{ MOISTURE} = \frac{(\text{ORIGINAL SAMPLE WEIGHT} - \text{DRY SAMPLE WEIGHT}) \times 100}{(\text{ORIGINAL SAMPLE WEIGHT})}$$

2. Sample weight calculation.

Sample weight required for dye analysis is calculated so that approximately 4 g of dry sample is analyzed.

$$\text{SAMPLE SIZE (GRAMS)} = \frac{400}{100 - \% \text{ MOISTURE}}$$

3. Preparation of calibration curve (required at least weekly).

- a. Prepare an aqueous 0.01% stock solution of ethyl violet dye by transferring 100 mg of ethyl violet dye to a 1000 ml volumetric flask that is then filled to volume with 50% v/v glacial acetic acid.
- b. Weigh the amount of dye-free (i.e., negative dye test in XX1) soda lime, calculated in XX3.3.2, in a plastic weighing dish and transfer that amount to each of four 100 ml volumetric flasks as quickly as possible. The dye-free soda lime must be from the same manufacturer as the samples to be analyzed.
- c. Add 80 ml of 50% glacial acetic acid to each flask. Retain one flask as a blank.
- d. Pipet 2 ml of stock dye solution to the second flask, 4 ml to the third, and 6 ml to the fourth. Add a Teflon coated stirring bar to each of the four flasks and stir with gentle heat until the sample dissolves. Wash down the stir bars during removal and bring the flasks to volume with 50% glacial acetic acid. Shake the flasks to insure thorough mixing.

e. Prepare the spectrophotometer for use following the operating instructions. Rinse the cuvettes twice with each solution and then fill them.

f. Scan each of the four solutions from 400 to 700 nanometers (nm). Record the absorbance of the peak maximum between 525 and 600 nm as A_{peak} and the baseline absorbance as A_{700} .

g. Calculate the delta absorbance (ΔA),

$$\Delta A = A_{\text{peak}} - A_{700}$$

and construct a calibration curve by plotting ΔA on the Y axis versus percent dye on the X axis. Each 2 ml of stock solution added is equivalent to 0.005% dye, by weight, for a 4 gram sample of soda lime (i.e., the X axis coordinates for the 4 flasks are: 0, 0.005%, 0.010%, and 0.015% dye). Connect adjacent points with straight lines. The calibration curve may or may not approximate a linear relationship, and may or may not go through the origin, depending on the composition of the soda lime that is being analyzed. ΔA for 0.005% dye must be at least 0.03 A.

h. A separate calibration curve needs to be made for soda lime samples from each manufacturer by using dye-free absorbent from that supplier.

4. Percent dye of soda lime samples.

a. Weigh the amount of sample calculated in paragraph XX3.3.2 to the nearest 10 mg in a plastic weighing dish and transfer to a 100 ml volumetric flask as quickly as possible. Do the same for a sample of dye-free soda lime from the same manufacturer to generate a blank.

b. Add 80 ml of 50% glacial acetic acid to both the sample and the blank and place Teflon coated stirring bars in the flasks.

c. Place the flasks on stirring hot plates and stir with gentle heat until all of the soda lime is dissolved. Do not allow to boil. Cool the flasks to room temperature. Wash down the stir bars during removal and bring the flasks to volume with 50% glacial acetic acid. Shake the flasks to insure thorough mixing.

d. Rinse the cuvettes twice with the sample and blank and then fill them.

e. Scan the sample and blank from 400 to 700 nm. Record the absorbance of the peak maximum between 525 and 600 nm as A_{peak} and the baseline absorbance as A_{700} . Calculate the ΔA as before.

f. Read the percent dye for the sample off the calibration curve for that manufacturer. Results will be reported to the nearest 0.001%. Any dye concentration that is 0.005% or

greater is unacceptable. Absorbance differences less than 0.03 A (including negative differences) are unreliable for quantitation, and the percent dye will be reported as "none detected (<0.005%)".

XX4. Quantitative determination of ammonia, diethyl amine, and ethyl amine in soda lime.

XX4.1. Principle.

This test measures ppmv levels of ammonia, diethyl amine, and ethyl amine in gas flowing from a bed of soda lime using infrared spectrometry. A method of equivalent sensitivity and accuracy may be used in place of that described. However, sampling of the headspace (gas space) inside soda lime buckets is not an acceptable alternative method of testing.

XX4.2. Equipment.

1. Soda lime bed chamber. This chamber is a plexiglas cylinder 23 cm in inner diameter by 27 cm in height with a stainless steel screen dividing the inside space into three compartments of approximately equal volumes. The total volume is 11.2 liters. The soda lime is placed in the middle compartment which allows for uniform gas distribution on the inlet and outlet side of the bed. The chamber top is removable for loading and unloading of soda lime.
2. The test apparatus is configured as in Fig. 2 using stainless steel fittings, valves, and 1/4 inch (outer diameter) transfer lines. The water bubbler is a plexiglas cylinder 7 cm in inner diameter and 30 cm long, filled approximately halfway with distilled water. The apparatus shall be an open system so that flow leaving the bed is not recirculated but rather directed into the gas cell and then out into the atmosphere.
3. Model LI-6252 CO₂ analyzer with model LI-670 flow control unit, capable of measuring 0 to 1000 ppm CO₂; LI-COR, Inc., Lincoln, NE; or equivalent.
4. Model 1600 FTIR with heated, 20 meter gas cell and QUANT software; Perkin Elmer Corp., Norwalk, CT; or equivalent.
5. Triple-beam balance or electronic balance with capacity up to 5 kg and resolution of 10 mg; metal weighing container with cover to hold 3 kg of soda lime.
6. STEC model SGD-710 precision gas divider; Horiba Instruments, Inc., Ann Arbor, MI; or equivalent. This device allows blending of a known calibration gas with a diluent gas in 10 equal steps from 0% to 100% of the original concentration.
7. Six gravimetric primary standards for FTIR calibration, prepared in hydrocarbon-free air: 10 and 30 ppm ammonia; 5 and 10 ppm diethyl amine; 5 and 10 ppm ethyl amine; all certified to +/- 2% relative and in pressurized cylinders.
8. Gases for calibration of CO₂ analyzer: gravimetric primary standard of 500 ppm CO₂ in 21% O₂/balance nitrogen, certified to +/- 1% relative and in a pressurized cylinder.

9. Gas mixture of 5% CO₂ in hydrocarbon-free air, certified to +/- 10% relative and in a pressurized cylinder.
10. Hydrocarbon-free air in a pressurized cylinder.
11. Suitable high-purity regulators (with stainless steel diaphragm, 0-50 psig delivery pressure) for above gases and flowmeter for delivery of 5% CO₂ in air and hydrocarbon-free air at 5 l/min.

XX4.3. Procedures.

1. The FTIR shall be calibrated each day according to manufacturer's instructions using the QUANT software set up to measure 4 components: ammonia, diethyl amine, ethyl amine, and water. Spectra are recorded at 2 cm⁻¹ resolution from 4000 cm⁻¹ to 700 cm⁻¹ with calibration windows 1200 to 800 cm⁻¹. All 6 gas primary standards are used so that a low and a high calibration is entered for each of the first 3 components; 100% humidified air is used for calibrating water. All calibration and analysis shall be done with gas flowing at 5 l/min through the 20 meter gas cell.
2. The following tests shall be performed monthly to define the performance of the test system:
 - a. Analytical accuracy will be determined for ammonia and the amines using the STEC gas divider, primary standards, and 100% humidified air as the diluent gas with the gas flowing from the divider directly into the gas cell. Minimum accuracy will be +/- 1 ppm over the measurement range from 1 to 30 ppm for ammonia and from 1 to 10 ppm for the two amines.
 - b. Recovery of ammonia and the 2 amines following passage through the apparatus shall be determined by flowing each of high calibration standards (dry) at 5 l/min directly into the inlet side of the empty test chamber and measuring their concentrations in the 20 meter gas cell after 10 min. Measured concentrations in the cell shall be no more than 5% below concentrations of the standards.
 - c. Baseline composition of the test apparatus will be determined by flowing hydrocarbon-free air through the water bubbler and empty test chamber and monitoring for ammonia and the 2 amines for at least 15 min. FTIR measurements shall be made at intervals no longer than 4 min apart. No ammonia or amines shall be detected (<1 ppm).
3. A soda lime sample of 2500 +/- 10 grams is poured from the supply bucket into a metal pan which is then covered with a metal lid and weighed on triple-beam or an electronic balance. Following weighing, the soda lime is poured into the test apparatus and apparatus sealed. These steps shall be completed in less than 10 min to minimize offgassing of the soda lime that might occur during loading.

4. Flow of 5% CO₂ in air is initially started at 5 l/min bypassing the soda lime bed and gas cell. Following at least 5 min of equilibration, flow is directed through the test chamber, into the gas cell, and is vented out to the atmosphere. Gas from the soda lime is monitored with FTIR for a minimum of 20 min or until the concentrations of ammonia, diethyl amine, and ethyl amine each are less than 1 ppm. Measurements shall be made at intervals no longer than 4 min apart. Gas flowing from the soda lime shall be periodically checked with the CO₂ analyzer to confirm removal of all CO₂ by the bed. Inlet and outlet flows shall also be monitored to check for leaks.

5. Maximum measured levels of ammonia, diethyl amine, and ethyl amine will be reported to the nearest 1 ppm and shall not exceed limits in Table X.

FIG. 1. IN LINE GAS TRAP

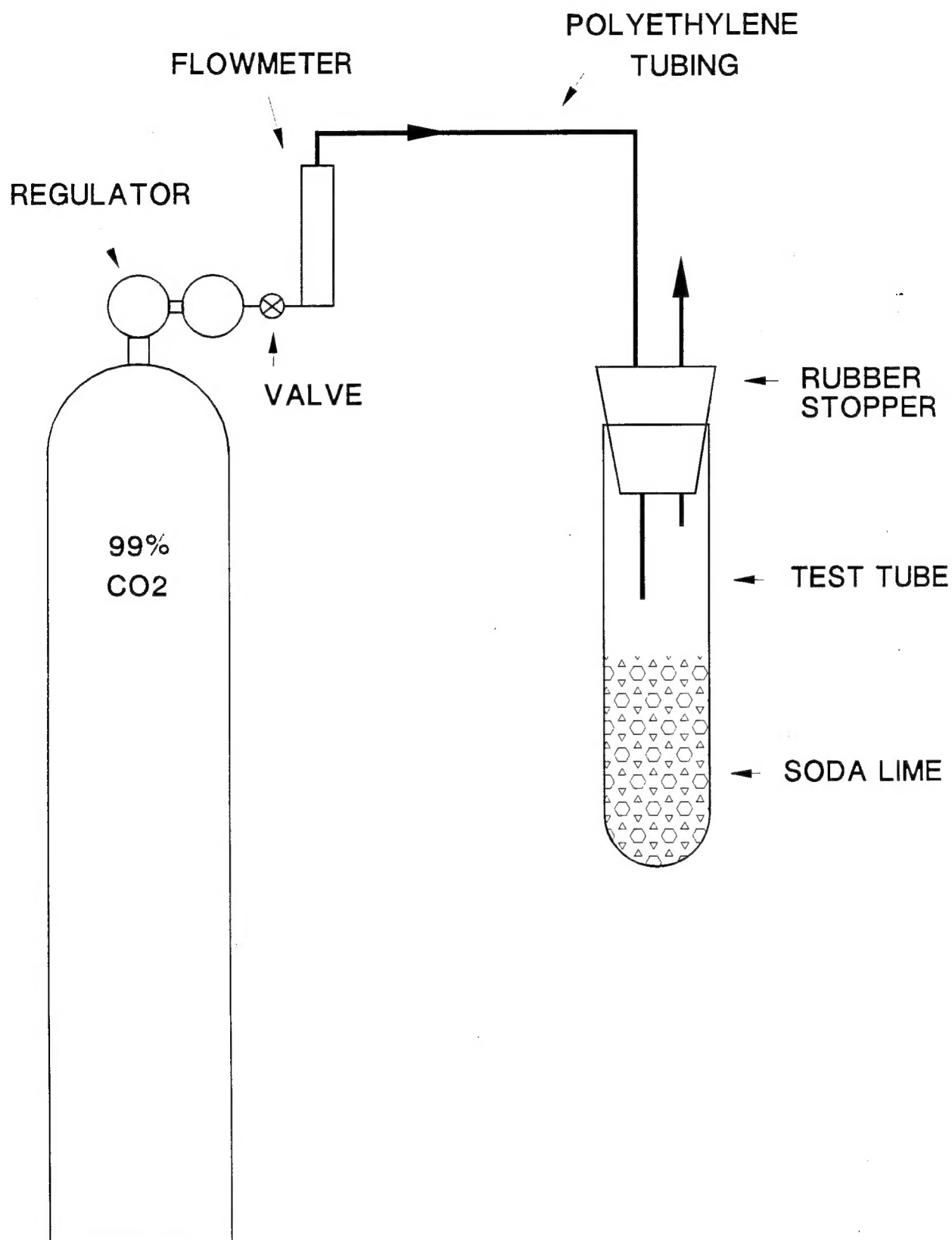


FIG. 2. TEST APPARATUS

